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DOUBLE KNUDSEN CELL SYSTEM FOR ALLOY ACTIVITY MEASUREMENTS BY

MASS SPECTROMETRY

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Abstract

A double Knudsen cell in conjunction with a high temperature mass spectrometer is one of the most versatile methods for direct, rapid measurements of alloy activities. Such an apparatus involves the use of a cell containing an alloy and a cell containing a pure metal mounted on the same flange, so that the two cells can be translated in and out of the sampling region. The major experimental problem in such an apparatus is molecular beam mixing, which is minimized with a novel system of shutters. Data for well-characterized alloys--Cu-Ag and Fe-Al--are presented to demonstrate the technique. Recent data on Ni-Al and Ti-Al alloys are also presented.

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## Introduction

High temperature mass spectrometry has been one of the most important techniques to obtain fundamental thermodynamic data for inorganic compounds (1). In these studies the material is placed in a Knudsen cell and heated. This allows equilibrium to be attained between a condensed phase and its vapor. A small orifice in the cell allows a minute amount of vapor to escape as a molecular beam for mass spectrometric analysis. The vapor composition, vapor pressures, and heats of vaporization can be obtained. The literature contains numerous studies of pure compounds conducted with this technique over the last forty years (2).

The technique can also be applied to multi-component systems as well. In general this is done by measuring the vapor pressure of a particular component in an alloy and comparing it to that in the pure compound. In a mass spectrometer, vapor pressure is related to ion intensity by (3):

$$P = kIT/\sigma\gamma \quad (1)$$

Here  $P$  is the vapor pressure,  $k$  is the calibration constant,  $I$  is the ion intensity,  $T$  is the absolute temperature,  $\sigma$  is the ionization cross section, and  $\gamma$  is the multiplier gain. In taking consecutive measurements on an alloy and a pure compound, it is necessary to maintain a uniform calibration constant. This involves maintaining precise alignment of the Knudsen cell and the ionization source and maintaining uniform characteristics of the ionization process. Some instruments are designed to do this (4,5); most are not (3).

Several methods have been developed to circumvent this problem of varying calibration constant. These methods have been discussed by Raychaudhuri and Stafford (6) and more recently by Kato (7), and will only be briefly summarized here. Perhaps the most common is the ion-current ratio technique, developed independently by Belton and Fruehan (8) and Neckel and Wagner (9). It has been applied to many binary systems and even some ternary systems. This method involves measuring the ion intensities of both components of the alloys across the entire composition range and taking their ratios. Then a Gibbs-Duhem integration is used to obtain alloy activities. Although this approach gives good precision, it is limited to alloys with measurable ratios over the entire composition, and a number of alloys over the composition range must be tested to perform the integration.

Another technique is the "monomer-dimer" method, where equilibria between the monomer and the dimer allows one to solve for the machine constant. This requires well-characterized monomer-dimer equilibria, which may not always be the case. Recently, a "valved Knudsen cell" technique (10) has been reported, which allows an alloy compound to be added in-situ and the subsequent activity measured. However, this method applies only to liquids where complete mixing occurs.

The most versatile approach to circumvent the variation in calibration constants and measure alloy activities is the use of an internal standard in a multiple Knudsen cell configuration. Although first demonstrated by Buchler and Stauffer (11) in 1966, only a few groups have further developed this technique (11-15). A pure reference material is put in one cell and the alloy in another cell. The activity is simply the ratio of the two ion intensities. In some cases the reference material may be different from the actual alloy constituents and appropriate

corrections for the cross sections and multiplier gain must be made. The multiple cell approach allows activities to be measured rapidly and directly for any component with sufficient vapor pressure. Even multi-component alloys may be examined, and it is not necessary to examine the entire composition range.

There are, of course, many experimental difficulties with this approach. Both cells must be at exactly the same temperature and it must be possible to reproducibly position the cells in the sampling region of the mass spectrometer. Furthermore there can be no mixing of the molecular beams.

The mixing issue is the most formidable. Buchler and Stauffer (11), Johnston and Burley (12), and Camersi et. al. (13) appear to have enough separation of the cells and sufficient beam collimation to prevent mixing. Chatillon et. al. (14) have developed an elegant approach based on a series of small apertures so that the ionizer effectively sees only inside the cell. This approach not only prevents beam mixing but also eliminates possible surface diffusion and re-evaporation effects from the heat shields. Stickney et. al. (15) have minimized the mixing problem by using tubes attached to orifices of the Knudsen cells. In this case, care must be taken to avoid interactions with the tube walls.

Here our approach to a double Knudsen cell will be described. We have used a system of shutters to minimize beam mixing. To demonstrate this technique, activities were measured in two well-characterized alloys--Cu-Ag and Fe-Al. Our measured activities for these alloys show good agreement with literature values. In addition, aluminum activities in selected Ni-Al and Ti-Al alloys are reported. There are only limited data in the literature on these two alloys. Since the Ni and Ti vapor pressures are much lower than the Al vapor pressures, the ion current ratio technique is not suitable for these alloys. Only the multiple Knudsen cell technique is applicable.

#### Experimental Procedure

Our double Knudsen cell apparatus is described in a previous paper (16) and will only be briefly summarized here. It was used in conjunction with a 90° magnetic sector mass spectrometer (Nuclide/MAAS/PATCO, Bellefonte, PA), configured so that the molecular beam, ionizing electrons, and ion beam were all mutually perpendicular. This allows direct sighting into the Knudsen cell with an optical pyrometer. This pyrometer was also used as a telescope to observe the cells as they were moved into the sampling region. A diagram of the entire apparatus is shown in Figure 1.

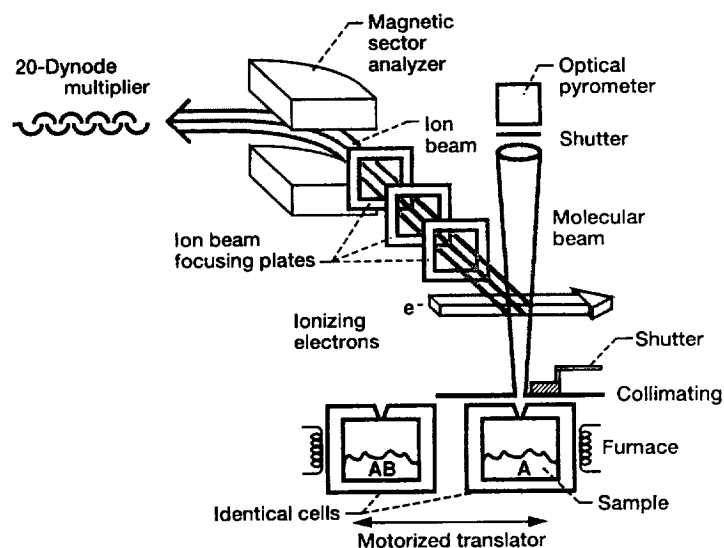


Figure 1. Schematic of Knudsen Cell mass spectrometer with double cell.

A detailed diagram of the Knudsen cell flange is shown in Figure 2. The Knudsen cells were mounted in a tantalum block, which minimized thermal gradients. Depending on the alloy, either graphite, alumina, or yttria stabilized zirconia cells were used. Heating was accomplished with a tantalum heating element and low voltage, high current power supply. Temperature was fixed by setting a voltage--no feedback loop was used. As mentioned, temperature was measured by sighting into the cell with a disappearing filament pyrometer (Pyrometer Instrument Co., Northvale, NJ). Temperature was calibrated from the melting points of Ag, Cu, or Au. The temperature was ramped and the onset of an arrest in ion intensity was taken as the melting point.

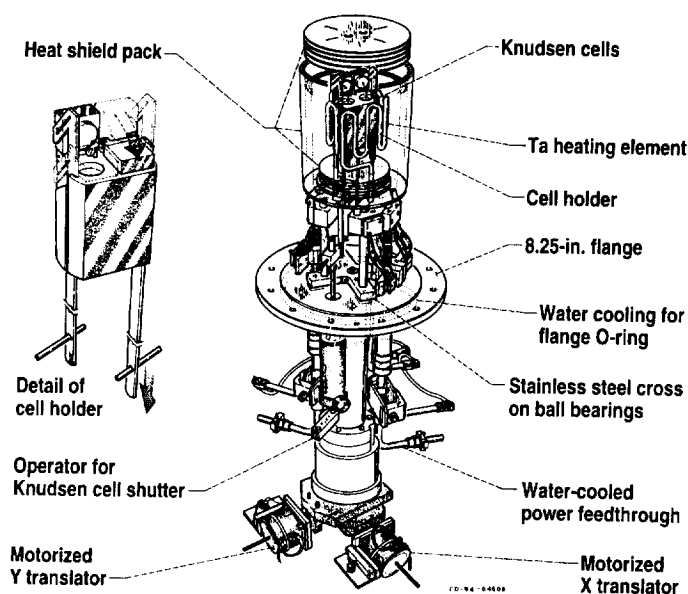


Figure 2. Schematic of double cell flange.

The entire furnace and cell assembly was translated by a commercial x-y motion feedthrough, as shown in Figure 2. Stepper motors were added to the feedthrough, which were controlled with a "joystick". This "joystick" was used while observing the cells through the pyrometer telescope as they were moved in and out of position.

Mixing of the molecular beams was minimized by the use of shutters over the cells, as shown in the detail in Figure 2. These were operated at temperature by push-pull motion controllers from the outside of the vacuum system. The moving parts were lubricated with a suspension of graphite in isopropyl alcohol. At high temperatures the alcohol vaporizes and leaves a graphite film.

Even with the shutters, some limited mixing did occur. This was measured by putting the pure standard in position 1 and an empty cell in position 2. The signal from position 2 was measured with shutter 1 closed and shutter 2 opened--this was the amount of mixing. Depending on the standard it was as high as 2% of the full signal of the standard. This was not a problem in the measurement of higher activities. However, for activities less than about 0.10, it was necessary to use another standard such as Au. The necessary corrections for ionization cross section and multiplier gain were made.

The mass spectrometer used an electron impact ionizer set for 18 eV electrons and 1 ma total emission. Ion were accelerated at 10 kV into a magnetic analyzer, set at 1200 resolution. This

was sufficient to separate the background hydrocarbons from the inorganic peaks. Ion currents were measured with a 20 dynode electron multiplier at gain of  $10^5$  and analog measurement.

### Results and Discussion

Results for selected alloys from the Cu-Ag, Fe-Al, Ni-Al, and Ti-Al systems are presented. As mentioned, the first two systems were studied simply to demonstrate the technique, since good data is available for these alloys.

The Ag-Cu alloys were prepared in-situ from high purity Cu and Ag in a graphite cell. A silver reference was used and the silver activity measured. The alloys were taken above their melting point and cooled to 1310 K for measurement. At this temperature, the Ag signal was quite strong and easily measured in our mass spectrometer. The literature data (10, 17) was at higher temperatures and extrapolated to 1310 K via the equation:

$$\ln \left( \frac{a_{\text{Ag}}(T_2)}{a_{\text{Ag}}(T_1)} \right) = - \frac{\Delta \bar{H}_{\text{Ag}}}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \quad (2)$$

Here  $a_{\text{Ag}}(T_2)$  is the activity of Ag at temperature  $T_2$ ,  $a_{\text{Ag}}(T_1)$  is the activity of Ag at temperature  $T_1$ ,  $\Delta \bar{H}_{\text{Ag}}$  is the partial molar heat of Ag at this composition, and  $R$  is the gas constant. Table I compares our data to activities extrapolated from the compendium of Hultgren et. al. (17) and from the measurements of Howard (10). In general, agreement is good.

Alloy Composition $x(\text{Ag})$	$a(\text{Ag})$ --this study	$\Delta \bar{H}_{\text{Ag}}$ -- Hultgren et. al. (17) J/mol	Extrapolated $a(\text{Ag})$ --Hultgren et. al. (17)	Extrapolated $a(\text{Ag})$ -- Howard (10)
0.15	$0.391 \pm 0.001$	11966	0.387	0.358
0.373	$0.616 \pm 0.012$	6778	0.634	0.606
0.61	$0.752 \pm 0.017$	3310	0.742	0.744
0.789	$0.821 \pm 0.016$	1155	0.842	0.836

Table I. Measured activities in Ag-Cu alloys at 1310 K as compared to extrapolated literature values.

To further demonstrate this technique, the aluminum activity in several Fe-Al alloys was measured. These were cast in a separate furnace and material from the center of the ingot was ground to a powder. Table II compares our results to those extrapolated from two studies in the literature. The partial molar heats were taken directly from the data of Eldridge and Komarek (18) and derived from the reported integral free energies of Radcliffe et. al. (16, 19). In general, good agreement is attained between our activity measurements and the extrapolated literature values.

Alloy Composition $x(\text{Al})$	$a(\text{Al})$ --this study	$\Delta H_{\text{Al}}$ --Eldridge and Komarek (18) J/mol	$a(\text{Al})$ --Eldridge and Komarek (18)	$\Delta H_{\text{Al}}$ --Radcliffe et. al. (19) J/mol	$a(\text{Al})$ --Radcliffe et. al. (19)
0.185	$0.011 \pm .001$	-86609	0.01	-79914	0.007
0.341	$0.042 \pm .016$	-69036	0.025	-76149	0.065
0.474	0.112	-53764	0.099	-58944	0.113
0.58	$0.255 \pm .005$	-47698	0.223	-44769	0.23

Table II. Measured activities in the Fe-Al system at 1410 K as compared to extrapolated literature values.

A partial molar heat can be calculated by measuring activity at several temperatures. This was done for the Fe-Al alloy with  $x(\text{Al}) = 0.474$  and the plot of activity vs.  $1/T$  is shown in Figure 3. The slope of this line is  $-62.8 \pm 5.5$  kJ/mol, in reasonable agreement to that measured by other investigators, as shown in Table II.

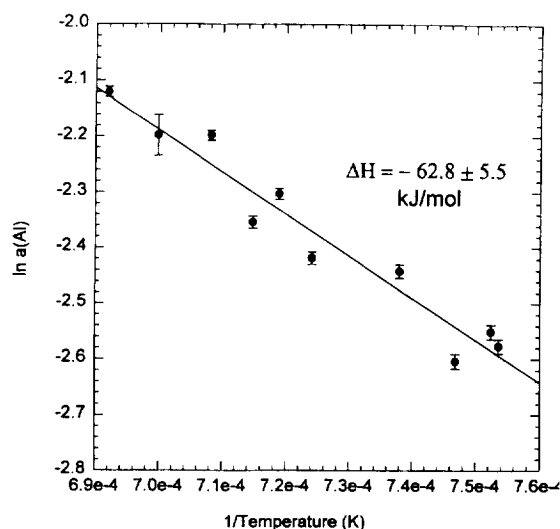


Figure 3. Plot of  $\ln a(\text{Al})$  vs.  $1/T$  for Fe-0.474Al to obtain partial molar heat.

Currently there is considerable interest in the intermetallic compounds in the Ni-Al and Ti-Al systems. However there is only limited activity data on these compounds. As mentioned, the large difference in vapor pressures between Ni and Al as well as Ti and Al makes them unsuitable for the widely used ion-current ratio technique. Therefore the multiple Knudsen cell approach is the only suitable mass spectrometric method for measuring activities in these alloys.

The high reactivity of alloys also makes cell material selection a critical issue. Yttria stabilized zirconia was chosen. After heat treatment in a low oxygen potential environment, this material becomes oxygen deficient and black in color. It appears to be inert to both systems.

The Ni-Al system is particularly interesting due to the large increase in activity across the  $\beta'$  NiAl phase. Thus in a study of Ni-Al thermodynamics, chemical analysis is particularly critical. Our initial results (20) for this system are shown in Table III. There are only three other studies over a wide composition range (21-23). Where possible, these have been extrapolated to our temperature of 1371 K. At the higher aluminum concentrations, a partial molar heat was not available and this extrapolation could not be done. However the activities show little temperature dependence at these concentrations. Our data shows reasonable agreement at some compositions and some inconsistencies at high aluminum compositions. Shaefer's data suggest near ideal behavior at high aluminum concentrations and our data tend to support this. This system is currently under study to further clarify the activity values at high Al contents and the large increase in activity across the NiAl phase field.

X(Al) and Phase Field	a(Al)--this study	$\Delta H_{Al}$ --Steiner and Komarek (21) J/mol	a(Al)--Steiner and Komarek (21)	a(Al)--Shaefer (22)	a(Al)--Oforka (23)
0.767--liquid	.620 $\pm$ .018				
0.73--liquid + Al <sub>3</sub> Ni <sub>2</sub>					0.35 (T=1423)
0.63--liquid + Al <sub>3</sub> Ni <sub>2</sub>				0.534 (T=1100)	
0.6--Al <sub>3</sub> Ni <sub>2</sub>		-25104	0.21		
0.561--NiAl	.303 $\pm$ 0.14				
0.55--NiAl		-71128	0.16		
0.353--NiAl	(3.55 $\pm$ 0.08) $\times 10^{-4}$				
0.35--NiAl <sub>2</sub>		-121336	1.43 $\times 10^{-4}$		1.49 $\times 10^{-4}$

Table III. Aluminum activity measured at 1371 K for selected Ni-Al compositions compared to extrapolated data from other investigators, where possible.

The Ti-Al system is another important system. However, there appears to be only one other previous study of this system (24) over the composition range of interest. Table IV lists our initial experimental data.



Composition x(Al)	Phase Field	This study a(Al)	Samokhval et. al. (24)
0.432	Ti <sub>3</sub> Al + TiAl	0.053 ± 0.01	0.017
0.53	TiAl	0.086 ± 0.005	
0.62	TiAl + TiAl <sub>2</sub>	0.177 ± 0.003	

Table IV. Aluminum activity data at 1391 K for selected Ti-Al compositions compared to extrapolated data of Samokhval et. al. (24).

### Summary and Conclusions

A double Knudsen cell mass spectrometer system has been described. Such a system is one of the most versatile ways of taking direct, rapid measurements of activities in alloys. The major experimental issue with this type of system is molecular beam mixing. This is minimized with a novel system of shutters. For measurements of very low activities, another standard such as gold is used and the necessary cross section and multiplier gain corrections are made. The use of the system is illustrated with well-characterized alloys of Ag-Cu and Fe-Al. Measurements on selected Ni-Al and Ti-Al alloys are also reported. Activities in the latter systems cannot be measured via other mass spectrometric techniques and are particularly suited to the double cell approach.

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